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RECOMPRESSION PHENOMENA IN STEAM NOZZLES[1]

PART I[1]

BY CHARLES ALEXANDER ROBB[2]

Abstract

The purpose of the investigation was to find when and how recompression occurs in the flow of steam through a nozzle, its causes and effects, how the results can be predicted, and what losses are caused by these phenomena. Four types of recompression were observed: equilibrium, latent, vena contracta, and shock recompression.

It is shown that steam in flowing through a nozzle of varying cross-section responds to the changes of area within certain limits and recompression phenomena may be expected. The Venturi effect has been observed in single nozzles, and in both parts of a composite nozzle.

The behaviour of steam in equilibrium recompression in convergent-divergent nozzles can be predicted by means of an equation from which a value is obtained for the pressure p_r at which overexpansion ends and an increase in pressure begins; the pressure p_r depends on the inlet pressure to the nozzle and on the difference in pressure at inlet and outlet.

The recompression due to the contraction of the section can be controlled and avoided by suitable provision in the design. The compression following a change of state of a flowing fluid can be controlled by adjusting the rate of expansion of the fluid in specified pressure ranges. Novel evidence of latent recompression is found in a break or notch in the pressure expansion curve plotted from search tube observations.

The experiments were carried out at inlet pressures within the range at which turbine-condition curves may cross the saturation line between the superheat and wet regions on the Mollier diagram, and the effects of recompression to be expected under varying load conditions can be interpreted for particular nozzle designs.

Comparative studies of the effect of the nozzle shape on recompression phenomena and the losses resulting therefrom have indicated that the conditions for favourable efficiency require a larger inlet radius at the throat and a length shorter than the lengths commonly found in practice.

I. Introduction

Recompression is the name given to certain secondary effects in steam flowing through a nozzle. Four types of recompression may occur in steam nozzles. The terms equilibrium, latent, vena contracta, and shock recompression, which characterize the respective phenomena, have been adopted. Examples of each of these types are to be found in the tests under review.

In *equilibrium recompression* the steam reaches its lowest pressure in the nozzle for fixed values of inlet and outlet pressure. Equilibrium exists between

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Condensed from a thesis presented to the School of Engineering, The Johns Hopkins University, in partial fulfilment of the requirements for the degree of Doctor of Engineering, 1937.

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the kinetic energy and the heat energy of the steam. As expansion proceeds in the steam flowing through the nozzle, the pressure falls, and the velocity V increases; the specific volume increases; consequently, the average density d decreases. It is found that the product of d and V at first increases and then decreases. The maximum product dV occurs at the section of the nozzle where the pressure bears a ratio of about 0.58 to the initial pressure. Up to this section, dV increases, and A, the area of cross-section, is made to diminish by making this portion of the nozzle convergent.

Supposing the nozzle to end at this section and the steam to be discharged direct from it into the exhaust chamber, the pressure in the exhaust chamber should be about 0.58 of the initial pressure for saturated steam and 0.54 for superheated steam, i.e., the same as that at the terminal section of the nozzle. Should the pressure in the exhaust chamber be less than this value, the pressure in the terminal section of the nozzle would be the same as before, but expansion of the steam would be completed by lateral spreading after discharge from the nozzle. To secure further expansion in the nozzle to a pressure lower than 0.58 of the initial pressure, the nozzle should be extended beyond the throat section. As the product dV is now diminishing, the area of the section must be increasing, hence the nozzle diverges in the portion beyond the throat, forming a diverging section. This portion is made conical in circular nozzles, the angle of the cone being about 10°. The cone must not diverge so rapidly that there is risk of the steam becoming separated from the sides of the nozzle. At all except the lowest exhaust pressures it is found that after expansion to some minimum pressure p_2, or recompression pressure to be discussed later, the process of reconversion of the kinetic energy to pressure energy takes place and the steam begins to recompress, discharging at approximately the exhaust pressure. When the pressure at exit from a nozzle is greater than the external pressure, the expansion is incomplete, and the nozzle is said to "underexpand" the steam. In this case the exit is too small. When the exit area is too large or the nozzle is lengthened, the steam expands below the pressure p_0 inside the nozzle and then rises to this value again at exit, that is, there is recompression. In this case the steam is said to be overexpanded. Equilibrium recompression is satisfactorily produced in each of the forms of nozzle used in the final series of tests.

Latent recompression follows undercooling or supersaturation. This is dependent upon the change of state of the water drops and the heat of vaporization or latent heat. It is regional and may be expected in the zone between the saturation and the 4% wetness line of the Mollier diagram. The steam is supercooled during expansion from the saturation line on the Mollier diagram down to the Wilson line, and a large number of drops of small size may be expected to form quickly at that point. The heat of vaporization from the condensation of the drops immediately becomes available, and tends to increase the temperature of the mixture of steam and drops, to decrease the density of the mass, and to speed up the velocity and hence the flow.

Vena contracta recompression occurs as the steam recovers from the effect of too quick a change of area at the throat or too small a radius in the converging portion of the nozzle. This effect gives the vena contracta at the throat of the nozzle and results in the jet leaving the wall in much the same way as a jet of water is reduced in cross-section as it leaves a sharp-edged orifice. As the recovery or recompression takes place, the jet refills the nozzle section. The effect may be expected in a nozzle having a very rapid reduction of area in the converging portion, or a short approach curve. There is an increase of pressure when the jet hits the wall after the vena contracta.

Shock recompression follows a sudden overexpansion due to shock or other disturbance to the flow. Such a disturbance may be caused by a slight roughness in the surface of the nozzle.

Certain of the above types of recompression may occur simultaneously, as, for example, latent recompression and vena contracta recompression.

In order to provide reliable information on recompression effects when using steam nozzles, it was decided to carry out a thorough experimental investigation in order to determine *(a)* when and how recompression occurs in the flow of steam through a nozzle, *(b)* its causes and effects, *(c)* whether and to what extent recompression can be predicted, and *(d)* what losses occur through recompression. The work was performed in 1931–32 at The Johns Hopkins University.

II. Description of Test Apparatus

(a) General Arrangement of Apparatus

Figs. 1, 2, and 3 show the main features of the apparatus. Fig. 1 shows the general arrangement of the apparatus; Fig. 2, the details of the search tube; Fig. 3, the details of the first nozzle form. Steam from the boiler was passed through the superheater S_1 (Fig. 1). This superheater was constructed of steel pipe, flanged and fitted with a spiral bronze coil. The core of the coil was sealed by means of a smaller pipe, plugged at the ends. High pressure steam entered the spiral coil through the valve V_3 and the condensate was discharged to the sewer through the trap T. This coil served to dry and superheat the steam supplied to the nozzle. The pressure of the steam supply to the nozzle was reduced by the main valve V_1 or by the by-pass valve V_2, or by both.

Steam at about 60 lb. per sq. in. absolute and 330° F. (30 degrees of superheat) was made to pass to the receiver R and the nozzle N, the pressure and temperature of the steam being observed by means of the supply gauge G_1 and the thermometer t_1. This arrangement of valves and superheater gave satisfactory pressure and temperature control of the initial conditions at the nozzle. Most of the steam supply to the nozzle was admitted through the main valve V_1, and the final adjustment of pressure was made by means of the small ($\frac{1}{2}$ in.) by-pass valve V_2.

The spiral path of the steam supply to the nozzle insured good contact with the superheater coil, and the temperature variation during an individual test was small. The receiver R was provided with a drip V_4 to clear the system of water during the warming up period.

The nozzle N was clamped between the flange of the receiver, which consisted of an extra heavy 2 in. tee, and the flange of the exhaust chamber H, which was also a 2 in. tee, by means of the studs Q, Fig. 2. The thimble T_3 was used as a distance piece since the over-all length of the nozzle assembly varied. Retaining grooves for the packing were cut in the ends of the thimble.

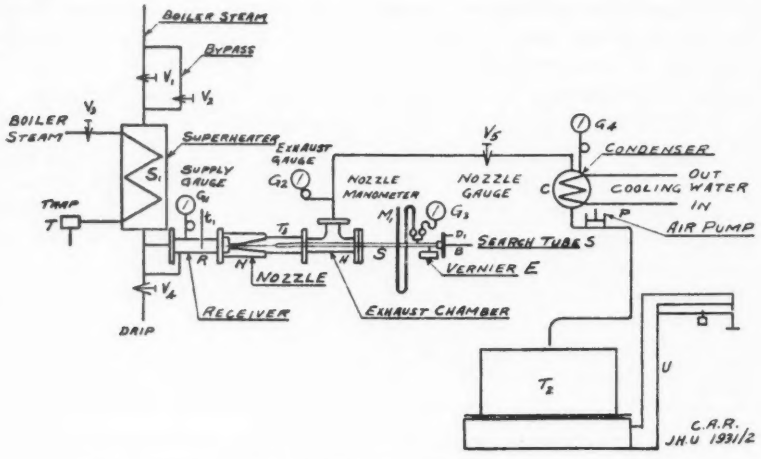


FIG. 1. *Arrangement of apparatus for the study of recompression of steam.*

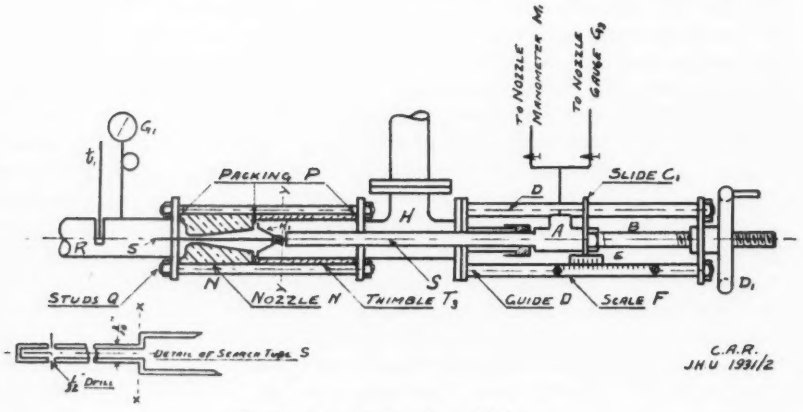


FIG. 2. *Construction of search tube.*

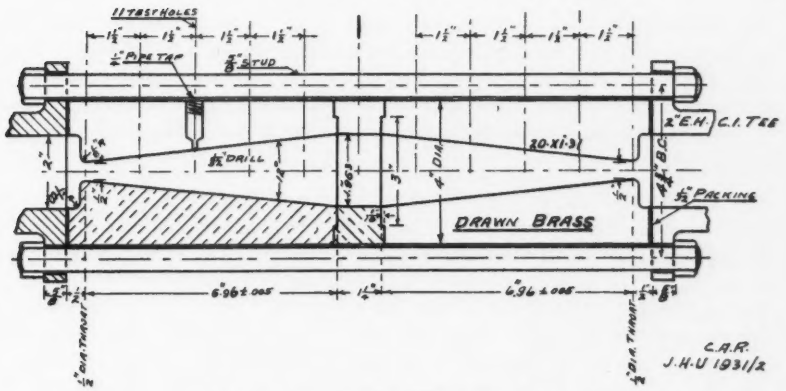


FIG. 3. *Convergent-divergent nozzle No. 1.*

(b) Measurement of Pressures

The *search tube* S, Fig. 2, consisted of a steel tube about $\frac{3}{16}$ in. outside diameter with a copper tube inside the steel tube. The copper tube had a bore of about $\frac{1}{32}$ in. A hole, $\frac{1}{32}$ in. diameter, was drilled diametrically in the tube. The outer end of the tube was sealed. This tube was brazed to the end of a $\frac{1}{2}$ in. o.d. brass pipe that served as a guide for the tube and as a means of transmitting the steam gauge pressure through the tee A to the nozzle manometer or to the nozzle gauge. The tee A was screwed on a solid threaded steel rod B, and a motion of translation was given to the search tube S by means of the handwheel D_1, the slide C_1, and the guides DD. The slide C_1 carried the Vernier E and this, in combination with the scale F, determined the position of the exploring hole in the search tube relative to the nozzle. The search tube S was supported concentrically at the nozzle by the spider H_1, which was fastened by means of screws to the nozzle. This arrangement provided a metal-to-metal contact between the spider H_1 and nozzle N as follows,—the plane of contact XX of the search tube S and the brass pipe was made to coincide with the plane YY of the spider H_1 (Fig. 2) and served as a datum from which the relative locations of the exploring hole, the outlet face of the nozzle, and the scale reading could be measured.

The pressure in the exhaust chamber H was controlled by means of the valve V_5, Fig. 1, and the pressure was observed by means of the exhaust gauge G_2. The steam from this chamber passed to the condenser C, Fig. 1, and the condensate was led to the tank T_2 on the platform scale U. When the exhaust chamber was to have subatmospheric pressures, the air pump P was used and gauge G_4 recorded the pressure in the condenser. The test instruments generally shown in Fig. 1 consisted of a barometer of the mercurial observatory type equipped with adjustment and thermometer, and pressure gauges G_1, G_2, G_3, and G_4 of the Bourdon single spring type. These were calibrated periodically during the whole program and immediately following

the final series of tests by means of a dead weight type of gauge tester. The manometer M_1 was used to record the lower pressures of the search tube. The condensation of vapour and heating of the mercury in the exposed leg of the manometer made it necessary to observe the initial and final difference of head at each new pressure reading and to apply corrections.

(c) Nozzles

Sketches of all the nozzles tested are shown in Figs. 4 to 13. All nozzles were circular in cross-section. The ***nozzle forms*** shown in Figs. 10 to 13, being those used in the final series of tests, were all cut from a single block of metal, and in such a way that the diverging part and the diameter of the throat remained unchanged for the set of nozzles Nos. 8 to 11 and similarly for the set Nos. 12 to 15. The radius of the approach was $\frac{1}{4}$ in. for nozzles Nos. 8, 12, and 11, 15, Figs. 10 and 13, and $\frac{1}{2}$ in. for nozzles Nos. 9, 13, and 10, 14, Figs. 11 and 12. The diameter of the throat was $\frac{1}{2}$ in. throughout and the length of throat was $\frac{3}{4}$ in. in nozzles Nos. 8 and 12, $\frac{1}{2}$ in. in nozzles Nos. 9 and 13, and nil in nozzles Nos. 10, 14, and 11, 15. The diverging portion was the same throughout each set of nozzles, i.e., Nos. 8 to 11 and Nos. 12 to 15, and was conical in form. The total angle of the cone was 6 degrees, each diverging side making an angle of 3 degrees with the axis. The length of the diverging part was 2.83 in., Fig. 10.

(d) Method of Operation

The superheating arrangements proved to be adequate. The warming up was quick and the inlet temperature, during a test, was nearly constant. The by-pass valve V_2 provided a sensitive adjustment for the inlet pressure to the nozzle. This arrangement made it easy to hold the inlet pressure at a constant value within the capacity of the Schaeffer and Budenberg single spring Bourdon gauge to indicate variations.

The steam supply pipe was insulated by means of asbestos covering, and, after the initial warming up period, a short time interval was sufficient for conditions to become steady.

The Vernier on the search tube was graduated to read in hundredths of an inch. The search tube was checked against a metallic stop after each test, as described above. This stop served as a reference point to the throat of each nozzle. The range of the search tube was $5\frac{1}{2}$ in., extending from the inlet to about $1\frac{1}{2}$ in. clear of the nozzle outlet. A constant inlet pressure of 59.2 psi abs., or about $44\frac{1}{2}$ psi (gauge) was chosen. The temperature range was from 300 to 315° F. in the series or about 30° F. above saturation temperature. The temperature variation during a test amounted to 1 to $2\frac{1}{2}$° F. from the average. Back pressures of 4, 14, 24, 34, 39, and 43 psi gauge, and a vacuum of 25 in. of mercury were adopted for the search tube experiments. A series of seven tests was carried out on each nozzle at constant inlet pressure and supplementary tests at an inlet pressure of 30 psi gauge and a back pressure of 14 psi, also at an inlet pressure of 15 psi gauge and 5 psi gauge back pressure.

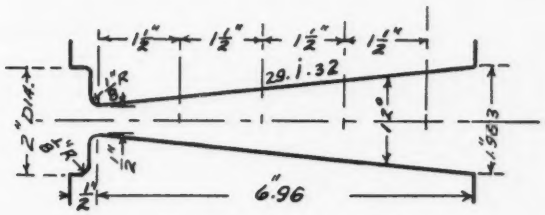


FIG 4 NO. 2

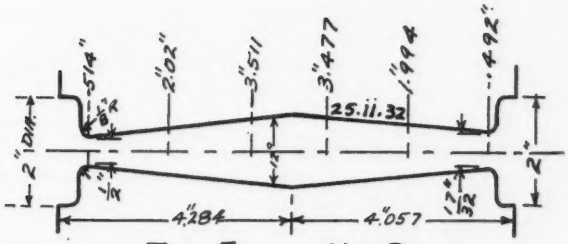


FIG. 5 NO. 3

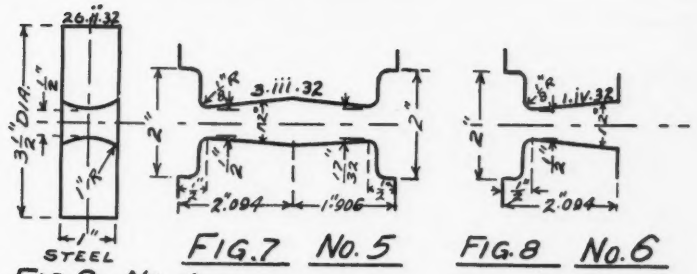


FIG. 6 NO. 4 FIG. 7 NO. 5 FIG. 8 NO. 6

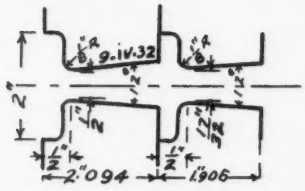
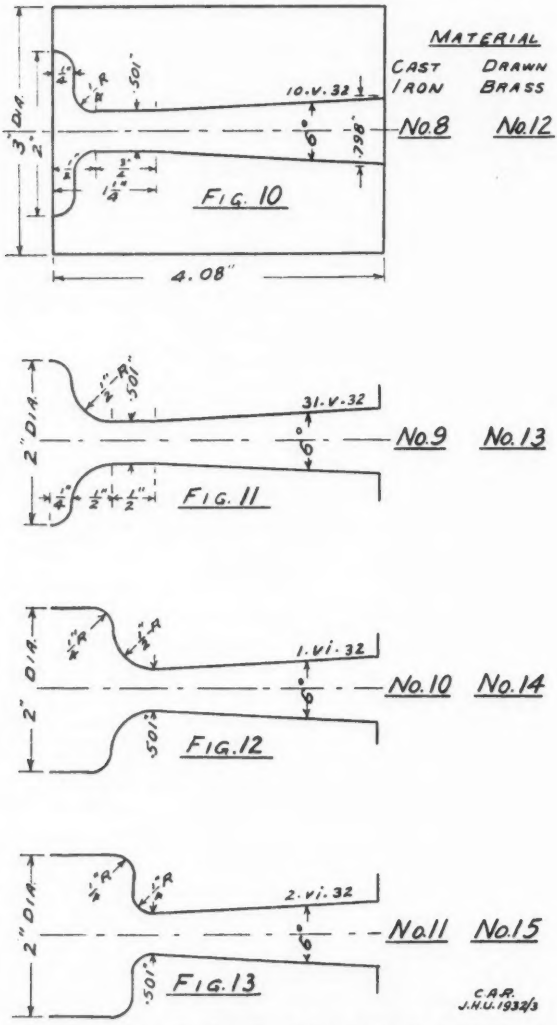


FIG. 9 NO. 7

C.A.R.
J.H.U. 1931/2.

FIGS. 4 – 9. *Nozzle forms. Axial cross-sections of nozzles No. 2 to No. 7, for the study of the flow of steam.*



FIGS. 10 – 13. *Nozzle forms No. 8 to No. 15 designed for the final series of tests.*

Pressure readings to the nearest 0.25 psi gauge or 0.1 in. of mercury (manometer) were taken at intervals of from 0.01 to 0.25 in. along the axis of the nozzle, the distance depending upon the importance of the region. The manometer was used for the low inlet and back pressures and for vacua. In changing from one instrument to the other, simultaneous readings were taken, thus providing a continuous check on the gauge.

The maladjustment of the mercury manometer due to thermal changes, condensation, and other influences was compensated at the beginning of each set of readings. At any indication of a break in the continuity of the observations, suggesting lack of stability in the static pressure, the search tube was backed up and the previous readings were checked.

The time, to the nearest second, at which the beam of the weight scale lifted clear was noted at the beginning and end of the test, and the net weight of the condensate was observed. An intermediate reading of time and weight was taken at about half-time, or a separate test was carried out. The duration of the test was governed by the capacity of the measuring tank at maximum flow. The duration of the other tests approximately correspond. Following the experiments, all gauges were checked by means of a dead weight gauge tester and the necessary corrections were made. The observed pressures, as ordinates, were plotted against the distance along the axis of the nozzle, as abscissae, after each test and before the remodelling of the nozzle for the next series.

At all points where a break, notch, or irregularity in the pressure expansion or recompression occurred, the pressure readings were observed a second time, confirmed for the doubtful interval, and so recorded. This notch, the author's observation of which was reported by Professor Christie (2), was the subject of very careful consideration throughout the whole investigation. Roughness of the surface of the nozzle was suspected as a possible cause for certain irregularities in the pressure readings, but it was found to persist even when the surface of the drawn brass nozzles was proved to be smooth.

In these nozzle experiments, a notch in the pressure-drop curve has been present in many of the pressure expansion and recompression curves. The inclination at first was to consider the notch as due to an error in observation, to a break in the continuity due to a surface irregularity, or to a lack of stability in the state of the steam. Even after what was expected to be the final series of tests had been carried out with cast-iron nozzles, the nozzle was cut in halves along the axis for inspection, and when it was found to have been pitted, the notch was the factor that led to a decision to repeat the whole series of tests with a new set of polished drawn brass nozzles.

Inspection of the cast-iron nozzle showed a faulty casting, and the pits and roughness were due to the combined effects of blow holes, oxidation, and erosion by the steam. None of these troubles developed with the drawn brass nozzles. The smoother surface of the drawn brass nozzles had the effect of permitting a greater overexpansion and of delaying equilibrium recompression. The effect was noted in the case of expansion curves for the outlet pressures 24 and 34 in Fig. 24 for nozzle No. 11. At a scale reading of 4.5 to 5 in. the two curves merged. The curves in Fig. 25 show the persistence of the notch in the curves obtained with the brass nozzles. The total weight of condensate observed in the tests of these nozzles amounted to 50 to 150 lb., according to the pressure drop. The duration of the test was from 364 to 1407 sec., and the rate of flow ranged from 0.0942 to 0.1496 lb. per sec.

III. Experimental Data

(a) Tests with Composite Nozzles

A question arose whether a specified recompression effect could be secured in certain apparatus. The question was:—"Following expansion of steam in a nozzle of conventional form (as in steam turbines), is an additional nozzle necessary to carry out a process of recompression, or would the addition, as the reverse of a Venturi meter, make the whole assembly constitute a simple chamber with no particular characteristics? Is it like adding two equal quantities, one negative and one positive?"

In order to study this question, it was decided to adopt the design of converging-diverging nozzle shown in Fig. 3, to provide two nozzles, and to insert a short cylindrical or parallel section between them. Test holes were drilled and tapped to receive gauges at the $\frac{1}{2}$ in. throat of each nozzle and at the centre as noted. These, with the pressures at the inlet and discharge chambers, gave five static pressure values along the axis. A series of observations was taken at inlet or supply pressures of 45, 30, 15 psi gauge and at various discharge pressures. For the 45 psi series the discharge pressures were 4, 14, 24, 34, 39, and 44 psi gauge. The pressure observations showed the effect on the static pressure of the variable cross-section. The pressure dropped at the first throat, increased as the cross-section increased, dropped again at the second throat and continued to expand to the receiver pressure. The limit of the pressure drop at the second throat was reached at a pressure in the outlet receiver of about 14 psi. Similar effects were found at the lower inlet pressures of 30 and 15 psi gauge.

The observations indicated that this combination of nozzles would serve to show the characteristics of a channel of varying cross-section; cocks were installed at points along the nozzle, and connected by a pipe manifold to a gauge and manometer. Pressure-flow tests were made with various inlet pressures (100, 45, 30, or 15 psi) and different discharge pressures. Evidence of a limiting critical pressure was found at the throats. In the case of the lower back pressure there was a striking disposition for the recompression pressure to reach a similar limiting value at a point $1\frac{1}{2}$ in. from the throats. The variation in pressure in the major central section was small.

(b) Tests with Single Nozzles

To investigate the behaviour of a single nozzle, the nozzle, which we shall call the recompression nozzle, at the right of Fig. 3, and the cylindrical distance

TABLE I

PRESSURE SCHEDULE, PSI GAUGE, FOR NOZZLE NO. 2

Inlet	Discharge
45	37, 18, 5; vac., 10 in. of mercury
30	24, 10, 5; vac., 14 in. of mercury
15	11.5, 1.5, 0; vac., 24 in. of mercury

piece were replaced by a short section of 2 in. E. H. steel pipe, the ends of which were grooved to retain the packing.

The schedule of the pressure-flow tests is given in Table I. Similar schedules were followed with all the nozzles.

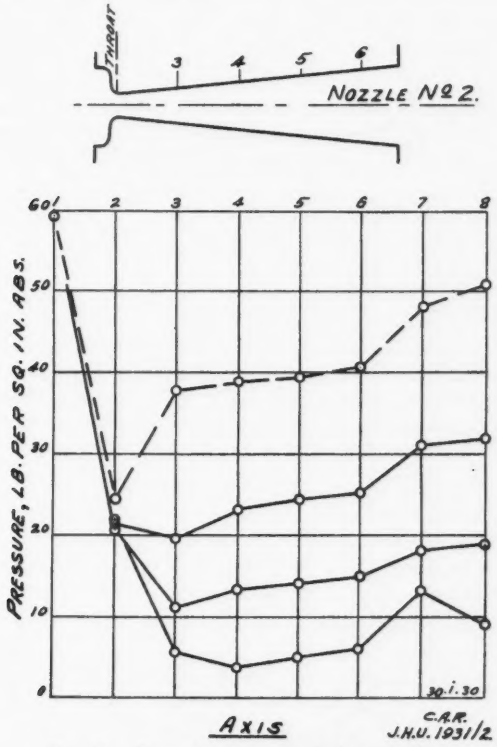


FIG. 14. *Recompression in the single nozzle No. 2.*

The pressure observations from the 45 lb. inlet pressure series are plotted in Fig. 14. All the curves except the curve for the highest back pressure show expansion at the throat to 7 to 7.5 psi gauge (21.6 to 22.1 abs.). The recompression is definite and regular. The single nozzle is providing recompression. This series of tests showed that the throat pressure p_t can be rendered unstable by a small change in the outlet or back pressure, as, for example, 37 psi gauge (51.6 abs.) when p_t is above the critical. It was observed that an increase of 1 psi in the back pressure raised the pressure at the throat by 4.5 psi.

Since the expansion is generally completed at from 1 in. to 2 in. from the throat, it would appear that the angle of divergence of the nozzle is excessive for the conditions under review.

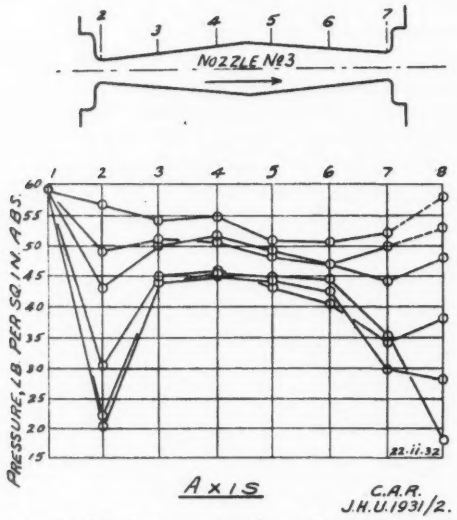


FIG. 15. *Effect of nozzle length on recompression. Inlet pressure 45, discharge pressure 44, 39, 34, 24, 14, 4 psi gauge.*

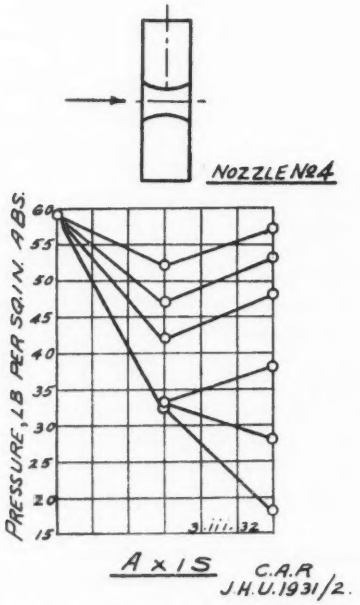


FIG. 16. *The Venturi effect in nozzle No. 4. Inlet and outlet pressures as in Fig. 15.*

In order to compensate for the losses in the nozzles, the throat of the recompression nozzle, shown at the right in Fig. 3, was opened out approximately 20% to $\frac{17}{32}$ in. diameter. The length of the nozzles was reduced, the distance piece or ring was omitted, and the nozzles reassembled as nozzle No. 3, shown in Fig. 5.

The pressure observations for the 45 lb. series are plotted, as ordinates, against the distance along the axis, as abscissae, in Fig. 15.

The need for the search tube, to permit pressure observations throughout the length of the nozzle assembly, became apparent at this stage. The construction of the search tube is shown in Fig. 2.

In order to study the behaviour of a single nozzle having easy converging and diverging sections, nozzle No. 4, shown in Fig. 6, was constructed of steel and erected with a distance piece consisting of 2 in. pipe.

The static pressure was read at the inlet, throat, and outlet only. The results are plotted in Fig. 16, which shows the effect of critical pressure.

The characteristics of nozzles No. 1, 2, 3, and 4 and the effect of nozzle form in producing recompression at various back pressures are shown in Fig. 17. The ordinates represent flow in pounds per second and the abscissae represent recompression pressures expressed in percentage of the inlet pressure $= \frac{p_0}{p_1} \times 100$.

It may be noted that the form of nozzle No. 2 is well adapted to a wide range of recompression with a minimum variation of the flow, as compared with nozzles No. 1, 3, and 4. Curve No. 2, Fig. 17, shows a recompression range of from 17 to 87%, the flow ranging from 0.172 to 0.167 lb. per sec.

The tests on nozzle No. 3, shown in Fig. 15, indicate that both the expansion and recompression nozzles are still longer than necessary for the pressure ranges under consideration, and the length was reduced to approximately 4 in. from throat to throat.

Nozzle No. 5, as remodelled, is shown in Fig. 7. Pressure-flow tests with the search tube were carried out at inlet pressures of 45 and 30 psi and a series of outlet pressures.

The pressures for the 45 psi inlet and 4 psi outlet condition are plotted in Fig. 18.

TABLE II

PRESSURE SCHEDULE, PSI GAUGE, FOR NOZZLES NOS. 6 TO 15

Inlet	Discharge
45	43, 39, 34, 24, 14, 4; vac., 7¾ in. of mercury
30	28, 25, 20, 14, 10, 5; vac., 12¾ in. of mercury
15	13, 10, 5; vac., 16 in. of mercury

These tests demonstrate that the process of overexpansion and recompression can be carried out on one nozzle only, and a series of tests was carried out on nozzle No. 6, a single converging-diverging nozzle.

The schedule of conditions is shown in Table II.

The pressures for the 45 psi gauge inlet and various discharge pressures are plotted in Fig. 19.

The two portions of nozzle No. 5 were placed in series, shown as nozzle No. 7 in Fig. 9 and the pressure-expansion curve, Fig. 20, indicates a repeated Venturi effect. The schedule of tests for this nozzle No. 7 and nozzles Nos. 8

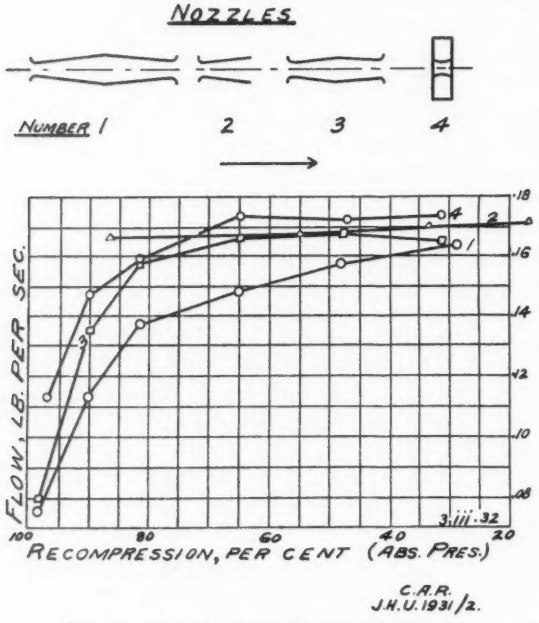


FIG. 17. *Flow tests for nozzles Nos. 1, 2, 3, and 4.*

to 15 is listed in Table II above, with the exception that the amount of vacuum varied slightly with the flow. Fig. 19 for nozzle No. 6 and Figs. 18 and 20 show the small length required to carry out a process of overexpansion and recompression.

(c) Final Design of Nozzles

An examination of the performance of the above nozzle forms was carried out with a view to the design of a final series of nozzles in which expansion and recompression processes could be controlled. For this purpose the nozzle is considered to consist of three parts, the converging, throat, and diverging portions, the form and functions of which will be considered separately.

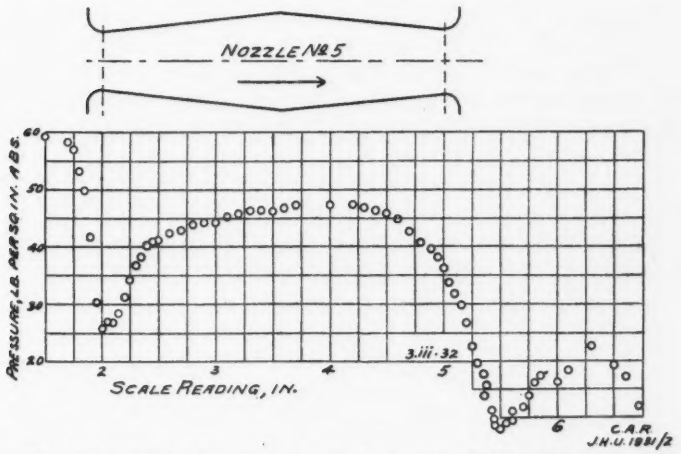


FIG. 18. *Recompression in composite nozzle of reduced length (No. 5). Inlet pressure 45, discharge pressure 4 psi gauge.*

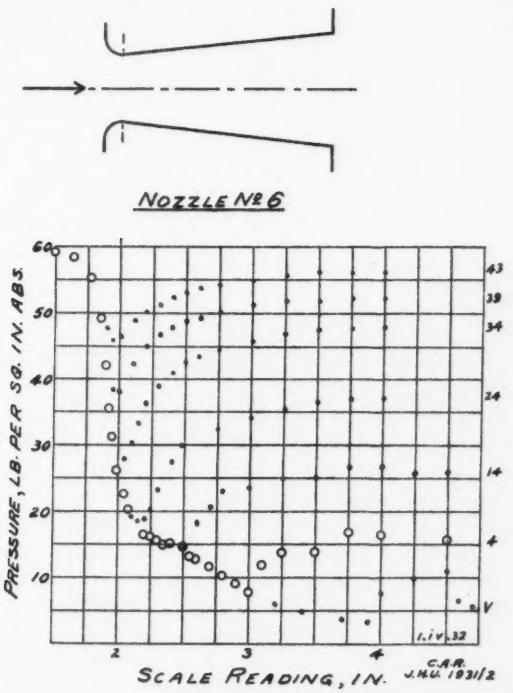


FIG. 19. *Recompression in single converging-diverging nozzle (No. 6). Discharge conditions are indicated in Table II.*

In the nozzles described above, preliminary expansion is rapid and the small inlet radius of $\frac{1}{8}$ in. rendered observation of a sufficient number of pressure values difficult. Radii of $\frac{1}{4}$ in. and $\frac{1}{2}$ in. were adopted, the smaller offering a satisfactory minimum and the larger radius serving to avoid the sharp edge or vena contracta effect, and to reduce the rate of expansion of the steam.

Further control of the rate of expansion and convenience of observation is obtained by the introduction of a parallel or extended throat section. This section provides a convenient location for suitable devices in case it is desired to separate the drops that form in the steam as it condenses.

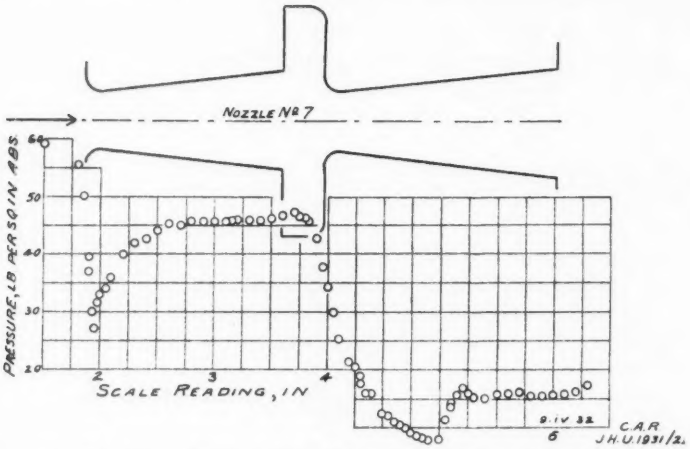


FIG. 20. *Pressure conditions in channel formed of the two portions of No. 5 in series (Nozzle No. 7).*

In order to obtain a more gradual recompression, the angle of the cone of revolution of the diverging section was reduced from a total angle of 12 degrees in the earlier designs to 6 degrees.

The cutting of the nozzles Nos. 8 to 11, constructed of cast iron, and of Nos. 12 to 15, of drawn brass, from a single piece of material, was executed in such a way that the original diverging section was retained in each of the succeeding models. The nozzle forms Nos. 8 to 15 are shown in Figs. 10 to 13 and specimen curves for each nozzle are shown in Figs 21 to 28. Nozzle No. 9 superseded No. 8 in order to remove the vena contracta effect noted at the point *A* in Fig. 21 due to the combination of the small entrance radius and to the parallel section. The notch in the expansion curve, an example of latent recompression, which is shown at *B* in Fig. 21, and which appears in each of the subsequent expansion curves, Figs. 22 to 24, occurs in the region of the Wilson line on the Mollier diagram, as indicated by the constant pressure line p_2 in Fig. 32. The parallel section or extended throat is omitted in

nozzles Nos. 10 and 11. The reduction in the rate of expansion at entrance, due to the larger ($\frac{1}{2}$ in.) radius and the parallel or extended throat, can be seen in Fig. 22 as compared with the smaller ($\frac{1}{4}$ in.) radius and more rapid expansion shown in Fig. 24. The cast-iron nozzles, Nos. 8 to 11, were found to have an unsatisfactory internal surface when split and inspected after

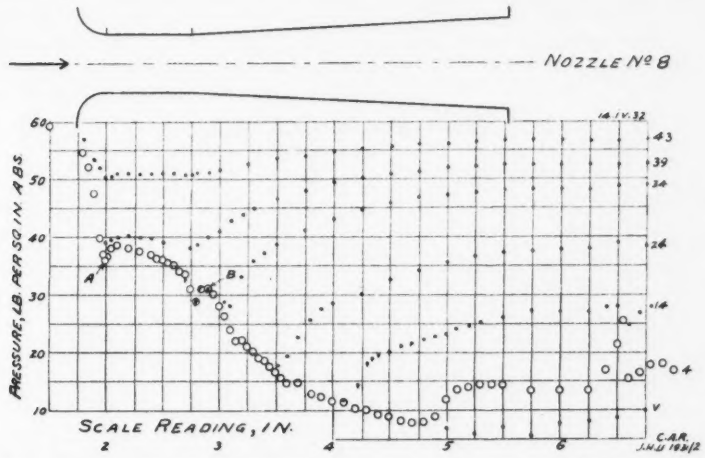


FIG. 21. *Vena contracta recompression at A in the single convergent-divergent cast-iron nozzle No. 8.*

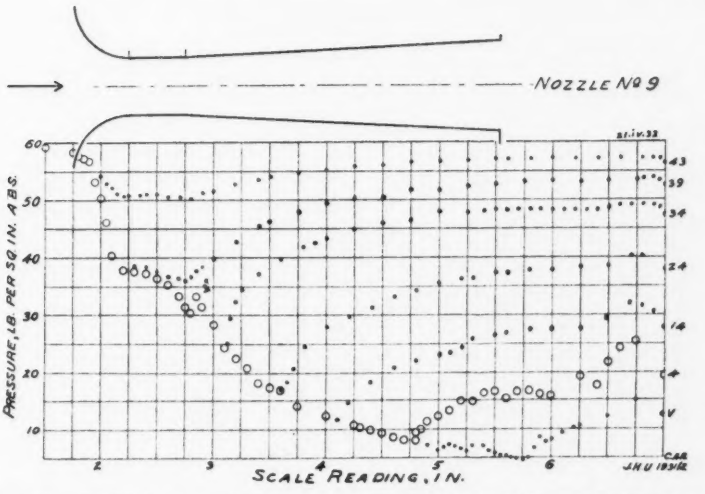


FIG. 22. *Equilibrium recompression in cast-iron nozzle No. 9 with increased inlet radius.*

the tests, and were superseded by drawn brass nozzles, Nos. 12 to 15, of the same design. Pressure expansion curves for nozzles Nos. 12 to 15 are shown in Figs. 25 to 28 respectively.

The effect of harmonic vibrations on the pressure expansion curves is shown in Fig. 19, Curve *V*, for nozzle No. 6, in Fig. 21, Curve 4, for nozzle No. 8, and in subsequent pressure expansion curves.

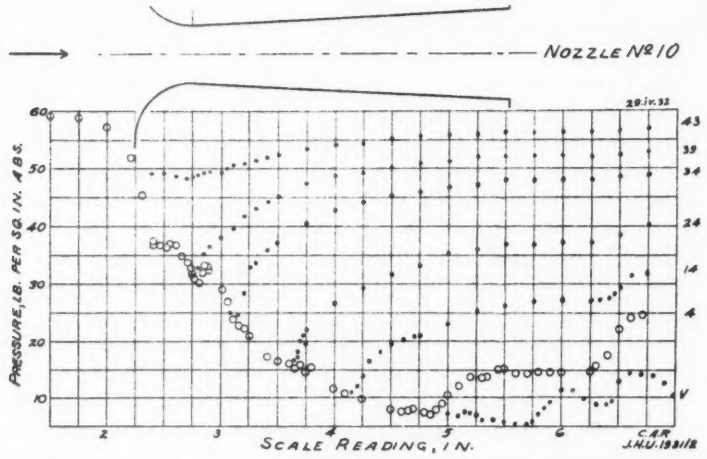


FIG. 23. *Example of shock recompression in the flow of steam for discharge pressures 14, 4, and V.*

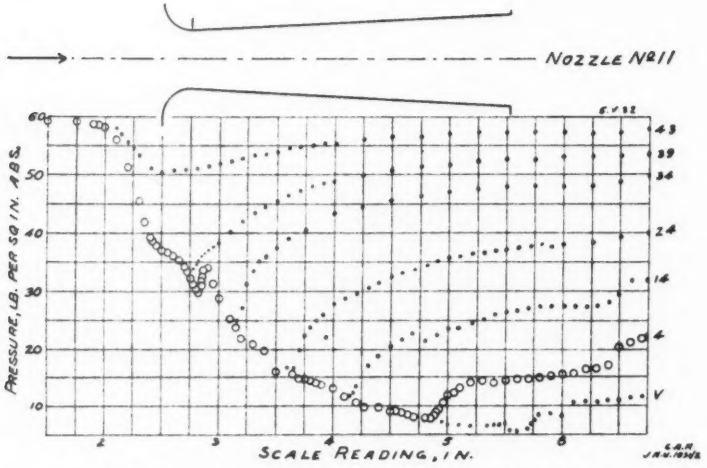


FIG. 24. *Latent recompression in cast-iron nozzle No. 11.*

The question formulated at the beginning of the section can be considered as answered, at least in part, by the tests on nozzle No. 1; i.e., the addition of the reverse of a Venturi meter does not make the assembly constitute a simple chamber with no particular characteristics. The pressure expansion curves show that the steam expands and recompresses in such a way as to indicate a direct relation, within certain limits, between the expansion and the cross-sectional area of the nozzle. The limits are fairly defined by Figs. 15 and 18 in which the lengths of the composite nozzles Nos. 3 and 5 are reduced as compared with nozzle No. 1.

(Part II will appear in the June issue.)

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THE DEHYDRATION OF TRICALCIUM ALUMINATE HEXAHYDRATE[1]

BY W. G. SCHNEIDER[2] AND T. THORVALDSON[3]

Abstract

Samples of the isotropic hexahydrate of tricalcium aluminate were dehydrated in a current of dry air at various temperatures up to 1050°*. The water retained and the lime liberated were determined. The results of earlier preliminary studies in this laboratory were confirmed. At low temperatures an isotropic hydrate of the composition $3CaO \cdot Al_2O_3 \cdot 1\frac{1}{2}H_2O$, having a refractive index of 1.543 ± 0.003, is formed. This hydrate is stable in dry air up to a temperature of approximately 275° and when once formed at lower temperatures has a very slow rate of decomposition below 350°. On continued dehydration above 275° decomposition occurs with the liberation of calcium oxide. Between 550° and 950° quantitative decomposition occurs into calcium oxide and an aluminate of the composition $12CaO \cdot 7Al_2O_3$. In the upper part of this temperature range prolonged heating causes slow recombination of the solid decomposition products, and above 950° this effect becomes marked. Dehydration of the hexahydrate in a current of dry nitrogen gives similar results. The experiments indicate that the system $3CaO.Al_2O_3 \cdot 1\frac{1}{2}H_2O$–$3CaO \cdot Al_2O_3 \cdot 6H_2O$ would serve as an efficient drying agent at temperatures below 100°.

In previous work in this laboratory (6) it was found that when the isotropic hexahydrate of tricalcium aluminate is heated in a current of dry air at temperatures below 275° to 300°, simple dehydration of the aluminate takes place with the formation of a hydrate of the composition $3CaO \cdot Al_2O_3 \cdot 1\frac{1}{2}H_2O$, while, on the other hand, heating at higher temperatures causes simultaneous dehydration and decomposition of the aluminate with the liberation of a part of the lime present. At still higher temperatures recombination of the two solid decomposition products occurs, so that the heating of the hydrate at 1000 to 1100° may show no ultimate liberation of calcium oxide, anhydrous tricalcium aluminate being produced. A recent study (7) has shown that this recombination is very slow if the temperature is kept below 850°.

Köberich (2) made a eudiotensimetric study of the dehydration of the hydrate over a wide range of temperature. He reported that between 180° and 260° the dehydration from $3CaO \cdot Al_2O_3 \cdot 6H_2O$ to $3CaO \cdot Al_2O_3 \cdot 1\frac{1}{2}H_2O$ is reversible and takes place without change in the crystal structure except that there is a shrinkage in the unit cell corresponding to a decrease in the

[1] *Manuscript received February 8, 1941.*
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.

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[3] *Professor of Chemistry.*

* *All temperatures in this report are given in degrees Centigrade.*

lattice constant from 12.542 to 11.94 Å. On the other hand, he found that dehydration below the $1\frac{1}{2}$-H_2O hydrate at temperatures between 400° and 500° is irreversible with destruction of the crystal lattice and liberation of lime. From this he concludes that 12 of the 48 molecules of water in the unit cell of the hexahydrate are present in the lattice in the form of OH groups.

Büssem (1, pp. 156–157) suggests that the behaviour on dehydration as outlined by Köberich may be explained by assuming that a transformation of $Al(OH)_6$ groups into $Al(OH)_4$ and AlO_4 groups takes place. This leads him to the assumption that a hydrate having 2 instead of $1\frac{1}{2}$ moles of water is formed. Büssem considers that Köberich's curves for the dehydration tend to give values approaching $1.8H_2O$ and support the assumption that the lower hydrate contains 2 moles of water.

Nacken (5) also made a eudiotensimetric study of the dehydration and came to the conclusion that hydrates having 4 and 2 moles of water are formed. During the dehydration of the dihydrate he found that lime was liberated, the maximum value obtained being 25.73% CaO after heating for three hours at 611°, while no free lime was found when the product was heated for three hours at 1260°.

Köberich (2) gives a critical discussion of the eudiotensimetric method of studying dehydration and shows how easy it is to come to misleading conclusions as to the composition of stable hydrates. The information as to experimental conditions given by Nacken (5) is hardly sufficient to determine whether he took the precautions that Köberich considers essential in order to obtain reliable results.

Lefol (3, 4) also studied the dehydration of the hexahydrate and found that below 260° the loss of water is very slow, while between 260° to 300° there is a very rapid increase in the rate. Between 315° and 350° a product of constant composition, $3CaO \cdot Al_2O_3 \cdot 1\frac{1}{2}H_2O$, was obtained under the conditions used.

Travers (8, pp. 225–226) and Travers and Zahabi (9) report that when the hexahydrate is heated in a current of nitrogen no loss in weight is shown below 175°; that, between 275° and 450°, 67% of the water is given off, the dihydrate being formed; that only towards 1000° is the dehydration complete and that no free lime is in any case obtained during the dehydration. These authors attribute the absence of free lime to the use of an inert medium (nitrogen).

The lack of agreement of the results obtained by different experimenters led the authors to conduct the present series of experiments.

Experimental

For the details of the preparation of the anhydrous tricalcium aluminate, the conversion of the same to the hexahydrate, the type of furnace used for the dehydration, and the precautions taken against contamination of the samples, the reader is referred to a preceding paper (7). The temperatures were measured by means of calibrated thermocouples; copper-constantan

being used for the low, iron-constantan for the medium, and platinum-platinrhodium for the higher temperatures. The temperature of the furnace remained constant to within $\pm 5°$ during a run. Attention should be drawn to the purification and thorough drying of the air circulating through the furnace. The air, in the form of small bubbles, was passed through a series of towers, packed with glass beads, countercurrent to a solution of caustic potash and sulphuric acid, then through a tower of soda-lime, while the last traces of moisture were removed by a long column packed with anhydrous magnesium perchlorate (10).

Dehydration at Low Temperatures

Several series of dehydrations of the hexahydrate at temperatures between 150° and 400° were made. In dehydrations below 200° the loss in weight was very slow (12 hr. at 200° caused a change from $6H_2O$ to $5H_2O$) and a temperature of 275° or higher had to be used in order to obtain a product of constant weight in a reasonable time. When the samples of the hydrate were heated rapidly by introducing them into the hot furnace at temperatures above 275°, somewhat erratic results were obtained. This was probably due to the violent evolution of steam, favouring hydrolysis and causing the sudden collapse of the crystal lattice. On the initial heating of a sample of the hexahydrate it was therefore placed in the cold furnace and the temperature raised gradually to the one desired. If the sample was to be reheated it was then introduced into the furnace at the temperature of the dehydration. In some of the series the samples were heated for various time intervals, each sample being used only once, while in other series the one sample was heated at a given temperature for successive intervals of time with intermediate weighings. In the first type of experiment the loss of moisture was more rapid for a given total time of heating and free lime was obtained at a lower temperature. Thus free lime was present after prolonged heating at 300° or even at 275° (after heating for 40 hr.) as shown by a pink coloration imparted to the solid by phenolphthalein. When the second method was used, the loss of water was somewhat retarded after one or two periods of heating and a product of almost constant weight was obtained at temperatures up to 350° before any free lime could be detected.

Table I and Fig. 1 give the results of a typical series of experiments using 0.5 gm. samples of the hexahydrate, the one sample being used for all the determinations at each temperature. On completion of a series at a given temperature the sample was tested for free lime.

The experimental data of Table I and Fig. 1 confirm the previous results obtained in this laboratory. In all the dehydrations between 275° and 325° the loss of water to below $1.6H_2O$ is comparatively rapid; below this point it is very slow, the product approaching a constant composition at approximately $3CaO . Al_2O_3 . 1\frac{1}{2}H_2O$. The lag in dehydration at this composition is noticeable even when the temperature is high enough to cause liberation of lime on prolonged heating (cf. 350° series). In no case was free lime detected in the product until the hydration had dropped below $1.50H_2O$. It would

TABLE I

DEHYDRATION OF TRICALCIUM ALUMINATE HEXAHYDRATE

Total time of heating, hr.	Moles of water retained at given temperature					
	275°	300°	325°	350°	375°	400°
¼						1.65
½				1.98		–
1	2.99	1.79	1.62	1.62	1.61	1.37
2	1.89	1.62	1.58	1.57	1.57	1.31
3	1.73	1.58	1.53	1.54	1.42	–
4	1.71	1.54	1.52	1.53	1.40	1.04
6	1.67	–	1.52	1.53	1.38	–
8	1.65	1.51	1.51	1.51	1.37	0.72
15	1.59	1.50	1.51	1.46	1.36	–
26	1.57					
50	1.53					
75	1.53					
Test for free lime	Negative	Negative	Negative	Trace[1]	Present[2]	Present[2]

[1] *The tests for free lime were made by transferring the platinum crucible with the sample into 60 cc. of an anhydrous alcohol-glycerine mixture (5 : 1) with phenolphthalein as an indicator and refluxing the mixture. In this case the solid turned pink while the solution remained colourless, the colour of the adsorbed phenolphthalein being changed to the alkaline tint.*

[2] *Although considerable amounts of free lime were present, the titration with a standard solution of ammonium acetate in absolute alcohol was not satisfactory. The lime was extracted from the solid very slowly and the end-point was very indefinite. This was always found to be the case with the partly dehydrated aluminate.*

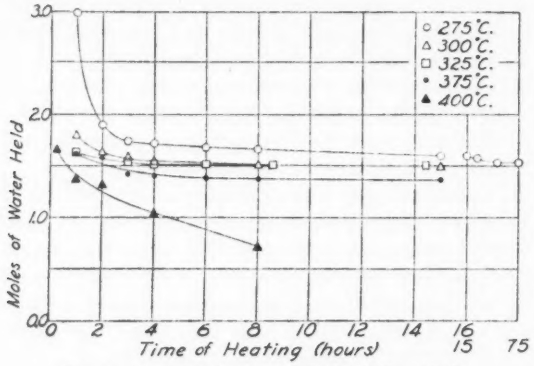

FIG. 1. *The dehydration of* $3CaO \cdot Al_2O_3 \cdot 6H_2O$.

therefore appear that this composition represents a definite hydrate of tricalcium aluminate and, also, as concluded by Köberich (2), the limit of the zeolitic dehydration. The refractive index of this isotropic lower hydrate was found to be 1.543 ± 0.003 (sodium light).

Dehydration at High Temperatures

Samples of the hexahydrate dehydrated at temperatures between 350° and 550° (and down to 300° when the heating was for one continuous long

period) always showed the presence of free lime when refluxed with the anhydrous alcohol-glycerine mixture. The quantitative determination of free lime in these products was, however, not satisfactory owing to the very long refluxing necessary and the uncertainty of the end-point of the titration. The qualitative test appears to be reliable, as a negative result under the same conditions was always obtained when the dehydration had not proceeded below the $1\frac{1}{2}$-H_2O hydrate. In addition X-ray powder patterns of dehydration products with less than $1\frac{1}{2}H_2O$ showed lines of CaO. This is in agreement with the results obtained with the product of dehydration over phosphorus pentoxide at 400° by Köberich (2, p. 17), who observed the lines of both decomposition products and in addition found 17.5% CaO by analysis.

Samples dehydrated at temperatures above 500° give consistent values for free lime, namely, a maximum of 26.7% CaO with the formation of an aluminate of the composition $12CaO . 7Al_2O_3$. Some recombination on prolonged heating is apparent but this is very slow at temperatures below 950°. The results of dehydration in this temperature range are given in a preceding paper (7). Above 950° the recombination to form anhydrous tricalcium aluminate is rapidly accelerated with increasing temperature. Samples of the hexahydrate heated in the furnace at 1050° for seven hours showed free lime absent.

Dehydration in an Atmosphere of Nitrogen

Dehydration of the isotropic hexahydrate in a current of nitrogen instead of air was also studied. The nitrogen was purified as described above for air. No difference in the behaviour during dehydration was discovered. Thus a sample of the hexahydrate after heating for one hour at 375° still held 1.4 moles of water. After further heating at 750° to 775° for three hours, 1.13% of water was held, and the sample was found to contain 26.4% of free lime. The authors are at a loss to explain the conflicting results of Travers and Zahabi (8, 9), unless the cause lies in the difference in the method of testing for the presence of free lime.

The System $3CaO . Al_2O_3 . 1\frac{1}{2}H_2O$–$3CaO . Al_2O_3 . 6H_2O$ *as a Drying Agent*

The experiments described in this paper show that air dried at room temperature by the very efficient drying agent, magnesium perchlorate, does not remove any water from the hydrate $3CaO . Al_2O_3 . 1\frac{1}{2}H_2O$ even when passed over the hydrate at temperatures up to 275° C. Further, the system $3CaO . Al_2O_3 . 6H_2O$–$3CaO . Al_2O_3 . 1\frac{1}{2}H_2O$ has a lower vapour pressure than the system CaO–$Ca(OH)_2$. The $1\frac{1}{2}$-hydrate of tricalcium aluminate when exposed to water vapour takes up moisture to the extent of 27% of its own weight to form the hexahydrate (2, p.17) and the $1\frac{1}{2}$-hydrate may be readily regenerated at 275° to 300° C. These facts indicate that the $1\frac{1}{2}$-hydrate of tricalcium aluminate is well suited for use as a drying agent. The great stability of the hexahydrate at 100° C. also indicates that the system $3CaO . Al_2O_3 . 1\frac{1}{2}H_2O$–$3CaO . Al_2O_3 . 6H_2O$ would be an effective drying agent at temperatures considerably above room temperatures.

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A NEW LOW PRESSURE GAUGE[1]

By C. C. Coffin[2] and J. R. Dingle[3]

Abstract

A heat-conductivity, low-pressure gauge based on the rate of sublimation of solid carbon dioxide is described. The gauge, which also serves as a trap in the vacuum line, is sensitive enough for most purposes. It is extremely simple and inexpensive to construct and operate.

Introduction

The fact that apparatus dimensions set an upper limit to the mean free path of gas molecules enables variations in the transfer properties of gases to be used for the measurement of low pressures. The Pirani-Hale heat conductivity gauge (3) and the Langmuir viscosity gauge (4, p. 107) are well known and thoroughly tested examples of such manometers. The present note describes a heat-conductivity, low-pressure manometer the operation of which is based on the rate of escape of gaseous carbon dioxide from a slush of solid carbon dioxide and ether. This gauge, which has been in use in this laboratory for several years, is very simple to construct and use. The fact that it cannot compete in precision with the more elaborate and expensive Pirani and ionization gauges is of no consequence in the many cases where a rough estimation rather than a measurement of the pressure is all that is desired. The fact that solid carbon dioxide makes a necessary and sufficient (if used with a phosphorus pentoxide tube (2, p. 74)) trap for both mercury and oil condensation pumps is a point in favour of this manometer, which of course also acts as an efficient trap. A distinct advantage is that since its range covers that of the McLeod gauge and even lower pressures it can be used in place of the latter in systems where the presence of mercury vapour is not desired. The functional disadvantages peculiar to the Pirani gauge are of course accentuated in this cruder variation of the instrument which has, however, the distinct advantage that no expensive corrodible auxiliary equipment is required.

Experimental

The gauge is shown in Fig. 1. The inner carbon dioxide chamber, A, and the outer air-stirred ice bath, B, are separated by the vacuum to be measured. The time taken for a given volume (20 to 50 cc.) of carbon dioxide to collect in a brine-filled gas burette (i.e., the time taken for a given change of liquid level in the burettes) is measured on a stop-watch and translated into pressure from a calibration curve made with a McLeod gauge and a pipette system (e.g., see (5)). A typical calibration curve is shown in Fig. 2. The bath

[1] *Manuscript received February 24, 1941.*
Contribution from the Department of Chemistry, Dalhousie University, Halifax, N.S.

[2] *Professor of Chemistry.*
[3] *Honours Student in Chemistry.*

must be stirred or a sheath of ice at an indeterminate temperature will form on the gauge at the higher pressures.

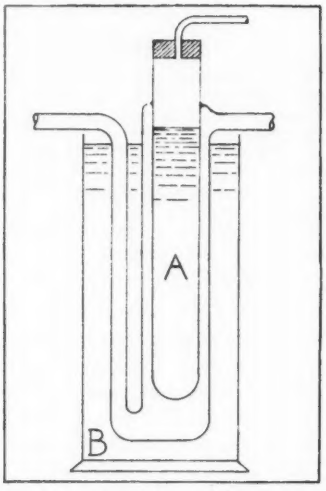

FIG. 1 *Carbon dioxide trap and pressure gauge.*

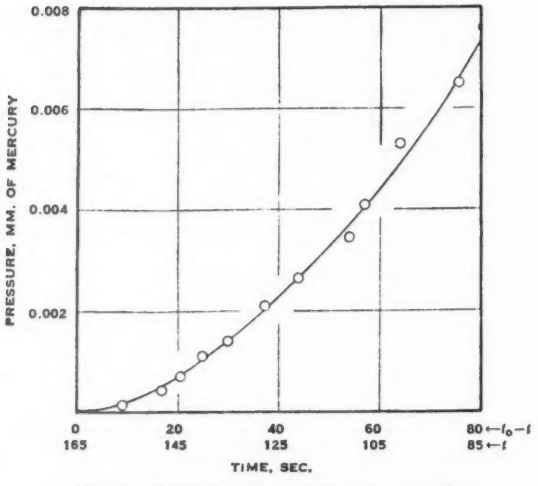

FIG. 2. *Calibration curve of pressure gauge No. 3*

The slush, which can be made with either "dry-ice" or carbon dioxide snow from a cylinder, requires rather careful preparation. It should contain as much carbon dioxide as possible and yet not be heavy enough to channel

clot or pack into wads with the gas evolution. A variation of several centimetres in the depth of the slush has no appreciable effect on the rate of escape of carbon dioxide for any given pressure in the gauge. At the higher pressures where carbon dioxide is being rapidly evolved frequent additions of solid carbon dioxide may be necessary. Measurements seem to be more reproducible if several minutes are allowed to elapse between readings. A multirange flowmeter has been used successfully in place of the gas burettes and, while not so sensitive as the latter, has the advantage that any sudden changes in pressure are instantly visible.

A typical calibration curve (Gauge No. 3: *A;* 3 by 26 cm.; *B*, 4.5 by 30 cm.) is shown in Fig. 2 in which pressures as measured with a McLeod gauge are plotted against time in seconds. The abscissa gives both t and $t_0 - t$, where t_0 is the longest time taken for a given amount of carbon dioxide to escape (i.e., the lower limit of the gauge) and t is the time taken for the same amount of gas at any pressure. The volume of carbon dioxide used in obtaining the curve shown was 50 cc. at a pressure of 76 cm. of mercury plus 40 cm. of brine. The fact that any gauge has the same value of t_0 with any reasonably good pumping system indicates that the gauge will not measure extremely low pressures and that its lower limit is in that pressure region where the energy conducted becomes negligible in comparison with that radiated.

Radiation to the carbon dioxide chamber may be decreased and the usefulness of the gauge extended to lower pressures by silvering the outer wall of *A* and the inner wall of *B*. A silvered gauge was found to take about twice as long to deliver a given volume of carbon dioxide at the lowest possible pressure as the same gauge before silvering. The outside of tube *A* of the gauge used in obtaining Fig. 2 was platinized (1) for use in the presence of mercury vapour. A narrow observation strip was left for observing the slush level. Subsequent removal of the platinum and total silvering increased t_0 by about 50%. An observation strip is not essential as the rubber stopper of *A* may be removed at any time and the slush level determined with a probe.

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THE OXIDATION OF *p*-NITRO-*p'*-HYDROXYAZOBENZENE AND SOME RELATED COMPOUNDS WITH HYDROGEN PEROXIDE[1]

By E. P. Linton[2], C. H. Holder[2], and H. E. Bigelow[3]

Abstract

p-Nitro-*p'*-hydroxyazobenzene, *p*-hydroxyazobenzene, and *p*-aminoazobenzene have been oxidized with 30% hydrogen peroxide. It has been found that in the case of the first two compounds prolonged treatment (25 hr.) disrupts both benzene rings and results in their complete oxidation to carbon dioxide, water, and nitrogen, or oxides of nitrogen. Oxidation of the third compound is not complete after six days.

Introduction

A number of instances of the direct oxidation of azo compounds to the corresponding azoxy compound are recorded in the literature (1–5, 7, 10). It has generally been found that oxidation is complete at this stage. Bamberger (8, p. 1953), however, observed that during the oxidation of both the α and β forms of *o*-hydroxyazoxybenzene with permanganate in a potassium hydroxide solution one benzene ring was removed and the final product was potassium isodiazotate. Angeli (6) obtained a similar result with the para isomer of this compound.

In an attempt by the authors to prepare the two isomeric azoxy compounds from *p*-nitro-*p'*-hydroxyazobenzene by treatment with hydrogen peroxide, it was found that on prolonged boiling the original compound entirely disappeared, being apparently oxidized to carbon dioxide, water, and nitrogen or an oxide of nitrogen. Since no case could be found in the literature in which a compound containing two benzene rings was completely oxidized in this way, it was decided to study the reaction quantitatively in order to determine the extent of the oxidation.

Experimental

A. Preparation of the Materials

Azoxybenzene was prepared by the action of sodium arsenite on nitrobenzene (9). This was treated with concentrated nitric acid at about 40° C. and the *o*- and *p*-mononitro derivatives obtained were readily separated by crystallization from alcohol, which yields the para compound in crystalline form. The ortho compound was obtained as an oil, which later solidified.

p-Nitroazoxybenzene was treated at about 100° C. for two to three hours with concentrated sulphuric acid. Under these conditions Wallach's rearrangement occurred, and *p*-nitro-*p'*-hydroxyazobenzene was formed. The resulting red solution was poured into ice and water. The insoluble product was

[1] *Manuscript received March 12, 1941.*
Contribution from the Department of Chemistry, Mount Allison University, Sackville, N.B
[2] *Instructors, at time of the research.*
[3] *Professor of Chemistry.*

filtered and then treated with ether, which eliminated a black powder consisting of polymerization products. The ethereal solution was extracted with 5% sodium hydroxide solution. *p*-Nitro-*p'*-hydroxyazobenzene was precipitated by acidifying the alkaline solution and was then recrystallized from alcohol. The product obtained was in the form of brilliant red or yellow flakes, which were purified by sublimation under reduced pressure.

The preparation of the *p*-hydroxyazobenzene was carried out by Wallach's rearrangement of azoxybenzene by a method similar to that described above. The *p*-aminoazobenzene was an Eastman Kodak Company product and was recrystallized from alcohol. The hydrogen peroxide was of 30% strength as supplied by Merck and Company.

B. The Apparatus

Fig. 1 is a diagram of the apparatus. *A* is the reaction flask, which is fitted with a ground glass joint, lubricated with phosphoric acid. The purpose of the silver wire in tube *G* was to decompose hydrogen peroxide vapour. *H* is a tube containing ignited wire-form copper oxide, at a dull red heat, used to convert carbon monoxide to carbon dioxide. *I* is a tube containing lead peroxide, which is heated in an oil bath at 185° ± 5° C. The

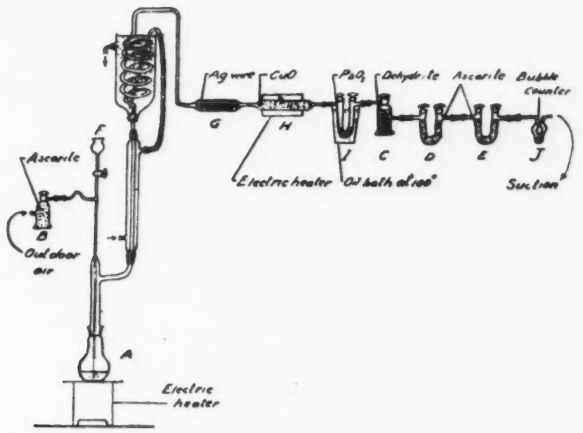

FIG. 1

lead peroxide was prepared according to Pregl's method, and was used to remove the oxides of nitrogen. Moisture was removed from the gases by tube *C*, which contains dehydrite. *D* is a weighing tube containing ascarite, and the progress of the oxidation was followed by observing the gain in weight of *D*; *E* is an ascarite tube that served as a check to determine if complete absorption of carbon dioxide was taking place in *D*. *J* is a bubble counter that gave an indication of the speed of gas flow.

In making a run, air was swept through the apparatus containing a weighed sample in *A* until the ascarite tube *D* gave a constant weight for four or five hours. The hydrogen peroxide was then added through the funnel *F*. The stopcocks at *F* and *B* were closed and the heater under *A* turned on. The evolved gases passed through the reflux condensers to the purifying train and the carbon dioxide constituent was absorbed in the ascarite tube *D*. The boiling hydrogen peroxide was coloured slightly by the red azo compound, which slowly dissolved and finally disappeared in six or seven hours. Suction was then applied at *J* and the evolved gases were slowly swept through the absorption train by allowing air to enter the system through the ascarite tube *B*. *D* was weighed at intervals and when it finally reached a constant maximum value it was concluded that oxidation was complete.

Results

Table I gives the results obtained in the oxidation of three closely related compounds. From the results listed it is clear that the first two compounds are completely oxidized by prolonged treatment with 30% hydrogen peroxide. It may be said that not all the results gave as good agreement as those listed. The unlisted results, however, showed no regularities among themselves so that it was concluded that those of Table I represent the normal results. Moreover, in most cases the anomalous results could be traced to the erratic behaviour of the lead peroxide. With a period of conditioning and proper

TABLE I

RESULTS

Run No.	Time required for weight to become constant	Weight of sample oxidized, gm.	Per cent oxidized
p-Nitro-p'-hydroxyazobenzene			
1	35 hr.	0.0567	100.5
2	30 hr.	0.0439	100.4
3	25 hr.	0.2365	98.1
4	40 hr.	0.1145	99.5
p-Hydroxyazobenzene			
5	35 hr.	0.1172	100.8
6	45 hr.	0.0849	100.7
p-Aminoazobenzene			
7	6 days	0.1279	Incomplete

temperature control of the bath surrounding the lead peroxide this difficulty was overcome. The lack in uniformity in the number of hours required for the weight to become constant is due to variation in heater temperatures and gas flow.

In order to show the progressive increase in weight of the ascarite tube, which finally reached a maximum as oxidation became complete, Table II has been included. This table gives the complete data for a typical run. The calculated gain for the ascarite tube is made on the assumption that complete oxidation to carbon dioxide occurs.

After refluxing the para aminoazobenzene for six days a small amount of a yellow solid of high melting point remained in the flask. On the other hand, the hydrogen peroxide solution left after oxidizing the other two compounds was water white and left no visible deposit on complete evaporation.

TABLE II

DATA FROM A TYPICAL RUN

No. of hours between weighings	Weight of ascarite tube, gm.	Total number of hours since adding H_2O_2
0	18.3953	
2	18.3960	
5	18.3962	
2	18.3963	
H_2O_2 *added*		
13	18.5053	13
6	18.5105	19
4	18.5147	23
5	18.5198	28
1	18.5198	29
2	18.5199	31
4	18.5200	35

Total gain in weight of ascarite tube $18.5200 - 18.3963 = 0.1237$ *gm.*
Weight of sample oxidized, 0.0567 *gm.*
Calculated gain if completely oxidized $\frac{528 \times 0.0567}{243} = 0.1231$ *gm.*
Per cent oxidized $\frac{0.1237}{0.1231} = 100.5\%$.

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PASTURE STUDIES. XXI.

AN IMPROVED THIOCHROME METHOD FOR THE ESTIMATION OF VITAMIN B_1[1]

By W. D. McFarlane[2] and R. A. Chapman[3]

Abstract

The thiochrome method as applied to foodstuffs by Pyke (10) has been modified to permit the use of the fluorimeter described by Froman and McFarlane (3). Interfering pigments are destroyed by adding hydrogen peroxide to the "blank" and test solutions before extracting with isobutanol. Hydrogen peroxide does not oxidize thiamine to thiochrome nor does it destroy the latter. The procedure described is based on a reinvestigation of the various methods proposed for extracting thiamine from tissues and also of the optimum amount of each reagent used in the thiochrome test.

The literature contains numerous recommendations for the modification of Jansen's method (5) for the estimation of thiamine (vitamin B_1), which is based on the measurement of the intense blue-violet fluorescence of its oxidation product, thiochrome. To separate thiamine from substances that interfere in the thiochrome test, Hennessy and Cerecedo (4) employed a base-exchanging zeolite (Decalso). Although recoveries of thiamine chloride of 91 to 97% are reported (4), it has become evident that the behaviour of "Decalso" adsorption columns is erratic, so that to obtain values approaching quantitative recovery the most exacting attention must be given to technical details, and "recovery checks" must be conducted with each assay and under identical conditions. According to Jowett (7) the recovery from pure solutions of vitamin is about 68% over a wide range of concentrations, and he has concluded that the loss is due to incomplete elution of the vitamin or to its destruction during elution.

Pyke (10) has applied the thiochrome test to foodstuffs by a method that omits the adsorption step, and this procedure seemed to be most suitable for the writers' purposes, namely, to investigate the thiamine content of pasture grasses. The analysis of grass by Pyke's method was attempted but in place of the prescribed visual-titration technique the writers employed the fluorimeter described by Froman and McFarlane (3). This instrument is of the compensating two-photocell type and had previously been found to perform satisfactorily when measuring the fluorescence of thiochrome solutions prepared from thiamine chloride. However, on applying the thiochrome test to grass extracts the final butyl alcohol solution was found to have a distinct greenish-yellow colour. The absorption of light by these pigments resulted in the "total blank" (ferricyanide omitted) giving a large negative reading

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when compared with the "reagent blank" (grass extract omitted). Repeated extraction with isobutanol, ethyl ether, or petrol ether, before applying the thiochrome test did not remove all the interfering pigments. Apparently some of the chromogens are extracted by isobutanol from strongly alkaline solution only, or they are formed by the action of strong alkali. Certainly their colour is intensified by alkali, and of course it is impossible to carry out a preliminary extraction with isobutanol from alkaline solution because of the known instability of thiamine. Even at pH 6 to 7, prior extraction with isobutanol resulted in some loss of thiamine; apparently, thiamine in neutral solution is slightly soluble in isobutanol. The colour of the test solution (ferricyanide added) was perceptibly less than that of the "total blank" owing to oxidation of the pigments. Furthermore, the addition of a known amount of thiochrome to the "total blank" gave a larger instrument reading than was to be expected. It was evident that the results would be too high if the estimations were made by adjusting the galvanometer to "zero" with the "total blank" and then reading the test solution; therefore, the "total blank" had to be reduced to a minimum and must not greatly exceed the reading of the "reagent blank".

Consequently, it was decided to investigate the method as applied to materials such as wheat germ, yeast, and flour, etc., the analyses of which have been reported by numerous investigators. The same difficulty was again encountered although to a lesser degree. It was found that the isobutanol extracts were colourless if hydrogen peroxide was added to the "blank" and "test" solutions before extracting with isobutanol, and the reading of the "total blank" was now virtually identical with that of the "reagent blank". This is true of all the analyses recorded in this paper, provided that methanol or ethanol is not present. Hydrogen peroxide does not oxidize thiamine to thiochrome, a fact that had previously been observed by Kinnersley, O'Brien, and Peters (8), nor does it destroy thiochrome, but in alkaline solution it rapidly oxidizes anthoxanthins and non-thiochrome fluorescing substances contained in the blank and test solutions.

The procedure that the writers are now using, as described below, is based on a reinvestigation of the various methods proposed for extracting the vitamin from tissues and also of the optimum amount of each reagent used in the thiochrome test.

Procedure

Grind solids as fine as possible to facilitate quantitative extraction of the vitamin. Transfer a 5 to 20 gm. sample, the weight depending on its thiamine content, e.g., 5 gm. of yeast or of wheat germ and 10 to 20 gm. of bread or flour, to a 250 ml. centrifuge bottle and add a 0.2% solution of pepsin in 0.33% hydrochloric acid (50 ml. to the 5 to 10 gm. sample and 75 ml. to the 20 gm. sample). Let stand for one hour, then adjust to pH 2.0 with *N* hydrochloric acid or *N* sodium hydroxide, using thymol blue as an external indicator, and incubate overnight at 37° C. Adjust to pH 4.5 with bromcresol green as an external indicator, add 0.1 gm. of takadiastase and incubate

at 37° C. for a further three to four hours. Centrifuge at maximum speed, transfer the supernatant to a 100 ml. volumetric flask and wash the residue twice with distilled water. Combine the extract and washings and dilute to volume with distilled water. At this point it may be advantageous, with some extracts, to further clarify a portion of the solution by filtering through a dry filter paper before applying the thiochrome test, which is carried out as follows:—

Pipette a 1 ml. aliquot of the extract into each of three 10 ml. graduated, glass-stoppered cylinders. The optimum amount of potassium ferricyanide in the test solutions varies according to the amount of organic matter present and, under the conditions prescribed here for 1 cc. of the extract, falls within a range of 0.1 to 0.4 ml. of a 1% solution. If 2 or 3 ml. of the extract is taken for the test, the optimum range of ferricyanide concentrations must be redetermined. To cylinders No. 1 and No. 2 add 0.2 and 0.3 ml., respectively, of a 1% aqueous solution of potassium ferricyanide. Dilute the contents of the three cylinders to 3 ml. with distilled water. Cylinder No. 3 contains no ferricyanide and acts as a blank. Add 1 ml. of 40% sodium hydroxide to each cylinder, mix thoroughly and let stand for two minutes. Add 1 ml. of 30% hydrogen peroxide, again mix thoroughly, and allow to stand for about five minutes. Add 5 ml. of isobutanol, stopper, and shake vigorously for one minute. Remove the stoppers and centrifuge at minimum speed (zero step on Q.V. circular rheostat), using the 250 ml. trunnion cups, containing the customary rubber pads. In addition, hold the cylinder in position with a No. 11 stopper bored so as to fit over the neck of the cylinder. Record the volume of the isobutanol layer.

Carry out the fluorescence measurements as follows:— Transfer a 4 ml. aliquot of each supernatant to three fluorimeter tubes (3) and add 1 ml. of 95% methanol to remove a slight turbidity due to moisture. Special care should be taken to ensure complete mixing, and the outside of the test tube should be perfectly clean. The writers have modified the procedure previously described (3) for making the readings. At least 15 min. before making a reading, switch on the ultra-violet lamp, with the galvanometer connected in the circuit. During that time a test-tube, painted inside with black enamel, is in the test-tube block and the polaroids are set at zero reading.

About five minutes before making a reading remove the blackened test tube and open the polaroids. Place tube No. 3 (which has not been treated with potassium ferricyanide) in the instrument, with the polaroids at zero and the resistance adjusted to give no deflection of the galvanometer. Replace the blank with one of the test solutions and rotate the polaroids until the galvanometer again reads zero. Record the polaroid reading and ensure that the voltage has not changed appreciably in the interim; this is done by replacing the test solution with the blank solution and observing that there is no deflection of the galvanometer at zero reading on the polaroids. If the results of the two tests do not agree closely, repeat the test making a small change in the volumes of 1% potassium ferricyanide solution. Calculate the

thiamine content of the solution by reference to a calibration curve (Fig. 1) or from the equation (3)

$$C = K' \sin^2 \theta,$$

where K' is a constant for the instrument and fluorescent substance which, by calculation from the data plotted in Fig. 1, is found to be 0.523 ± 0.021. With the higher concentrations of thiochrome, the fluorescence decreases rapidly in ultra-violet radiations and the polaroid reading should therefore not exceed 60. The observations on the thiochrome method which form the basis of this procedure are discussed below.

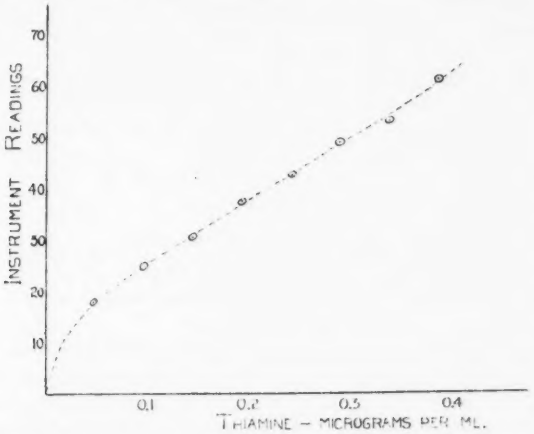

FIG. 1. *Relation between the concentration of thiamine hydrochloride and the fluorescence intensity of the corresponding thiochrome solution. (Tests conducted as described in text but with 0.2 ml. of 0.1% potassium ferricyanide.)*

Discussion

With the foods investigated, peptic digestion or incubation with hydrochloric acid alone under identical conditions gives virtually the same extraction of thiamine (Table I). Papain digestion as recommended by Emmett *et al.* (2) gives low results. These observations indicate that, in the extraction of thiamine, the pH is the important factor. However, peptic digestion may be advantageous, with some foods, as pointed out by Pyke (10), so that the simple addition of pepsin is adopted by the writers as a standard procedure. Less consistent results are obtained by refluxing and, with these products, autoclaving is definitely unsatisfactory. The data in Table I also indicate the reproducibility of the results obtained by the writers' procedure.

According to Booth (1), wheat contains little or no cocarboxylase so that, with wheat products, takadiastase digestion might be considered unnecessary. However, a clearer extract is obtained by this treatment, and it is probable that with some starchy foods it may be advantageous to use a longer digestion period than that recommended by the writers.

TABLE I

COMPARISON OF VARIOUS METHODS OF EXTRACTING THIAMINE FROM DIFFERENT MATERIALS
(Results expressed in International Units (micrograms × 3) per 100 gm.)

Method of extraction*	Dry yeast**			Wheat germ***	Special breads—Dried***	
	Number of determinations	Range	Average		*A*	*B*
I. Incubating at 37° C. for 12 hr.						
(a) Pepsin—HCl at pH 2.0	6	730–737	733	980	92	112
(b) HCl at pH 2.0	2	725–730	727	991	—	—
(c) Papain at pH 4.5	4	675–680	677	698	—	—
II. Refluxing for 1 hr.						
(a) HCl at pH 2.5	2	722	722	976	88	95
(b) CH_3COOH at pH 2.5	4	570–604	590	1023	66	90
III. Autoclaving at 120° C. for 40 min.						
H_2SO_4 at pH 3.0	2	360–397	379	446	—	—

* *Followed, in all cases, by takadiastase treatment at pH 4.5.*

** *Standard Brands Incorporated; Type 700-H; Guaranteed 600-900 I.U. per 100 gm.*

*** *Average of two determinations agreeing closely in each case. Bread A contained 5% wheat germ and Bread B was made from flour produced by a special milling process.*

In the earlier work the writers employed alcohol precipitation to reduce the organic matter content of the extracts, as suggested by Melnick and Field (9). Very satisfactory extracts are obtained when the takadiastase treatment is followed by the addition of 95% methanol to give a final concentration of 50 or 80% and provided that hydrogen peroxide is used in the thiochrome test. With yeast, wheat germ, and flour, the results are not significantly different from those obtained when the alcohol treatment is omitted. However, Johannson and Rich (6) find that in the analysis of flour this procedure greatly facilitates reading by the visual-titration technique.

Alcohol extracts of bran and grass give a large blank reading that is not satisfactorily reduced by the inclusion of hydrogen peroxide. For example, the apparent thiamine content of bran is 418 I.U. per 100 gm. when alcohol is employed and 214 when it is omitted. In the latter case, the blank reading is negligible and the value obtained is in good agreement with the average value obtained by bio-assay as recorded in the literature. This led the writers to investigate the common practice of adding alcohol in the thiochrome test, where it is said to stabilize the ferricyanide oxidation. The writers have found that the optimum amount of ferricyanide is not more critical when methyl alcohol is omitted, nor is the extraction of thiochrome by isobutanol diminished. Methyl alcohol facilitates the transfer of interfering pigments to the isobutanol layer and this is particularly evident with bran or grass extracts.

The amount of sodium hydroxide used in the test has been thoroughly investigated with extracts or pure solutions of thiamine and with varying concentrations of ferricyanide. Under the conditions of the test, maximum fluorescence is obtained with 1 ml. of 40 or 50% sodium hydroxide. Solid sodium peroxide can replace hydrogen peroxide in the test but it is less convenient. A larger amount of hydrogen peroxide than that recommended may be advantageous in some cases, but the writers have never found it advisable to reduce the amount. The test solution is extracted with an equal volume of isobutanol and the same ratio is employed in preparing the standard calibration data. Other investigators have used a larger proportion of isobutanol, usually 13 ml. to about 7 ml. of test solution. The writers have reduced the proportion of isobutanol so as to increase the sensitivity, having found that moderate variations in the ratio do not influence the amount of thiochrome extracted. The results in Fig. 1 are further evidence that, under the conditions of the test, sufficient isobutanol is being employed. The volume of extract may be varied but the amount of the reagents, including isobutanol, should be changed proportionately.

Two samples of bread analyzed by the writers' method or by a modification employing visual titration gave results that are of the same order as those obtained by bio-assay, whereas the introduction of Decalso adsorption gave results that are much lower (see Table II). This collaborative study is being

TABLE II

A COMPARISON OF THE THIAMINE CONTENT OF TWO SPECIAL BREADS* AS DETERMINED IN DIFFERENT LABORATORIES BY DIFFERENT METHODS

(Results expressed in International Units per 100 gm.)

Methods of analysis	Bread *A*	Bread *B*
Biological assay	99	113 and 130
Thiochrome method:		
(1) Decalso adsorption		
Laboratory *A*—photoelectric fluorimetry	58	78
Laboratory *B*—photoelectric fluorimetry	53	91
(2) Modified Pyke's Method		
Laboratory *C*—visual titration	86	132
Authors—photoelectric fluorimetry	92	112

* *See footnote—Table I.*

continued and extended to include other products. The writers' procedure gives equally satisfactory results (so far as the blank readings, etc., are concerned) when applied to beef liver, cabbage centre-leaves, carrots, and milk. Values of 105, 37, 36, and 15 international units of thiamine per 100 gm., respectively, were obtained; these appear reasonable when compared with the average values obtained by bio-assay as recorded in the literature.

Acknowledgments

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